

Report for 2003OH5B: The Effect of Humic and Fulvic Acids on Arsenic Solubility in Drinking Water Supplies

- Articles in Refereed Scientific Journals:
 - John J. Lenhart and Yaning Yang, 2004, Arsenic binding by natural organic matter, Manuscript in preparation for Applied Geochemistry.

Report Follows

The Effect of Humic and Fulvic Acids on Arsenic Solubility in Drinking Water Supplies

Interim Report

Statement of Critical Regional or State Water Problem

Arsenic in ground water results primarily from natural geochemical interactions that occur between water and As-containing rocks and minerals (Welch et al., 2000; Smedley and Kinniburgh, 2002). Due to its known toxic effects on humans, arsenic in drinking water is a threat to public health and is regulated in the United States by the Safe Drinking Water Act. On January 22, 2001 the United States Environmental Protection Agency (USEPA) published a Final Rule in the Federal Register (40 CFR 141.62(b)(16)) establishing a new maximum contaminant level (MCL) for arsenic of 10 µg/L, down from 50 µg/L. This revision reflects an improved understanding of the toxic effects of arsenic on humans, and is expected to decrease annual deaths from cancer by at least 20 (USEPA, 2002). On February 22, 2002 the new arsenic drinking water limit became effective. Enforcement of the Rule begins on January 23, 2006 and is expected to increase annual treatment costs by approximately \$181 million (USEPA, 2002).

Ground water is crucial to meeting the industrial and domestic needs of the residents of Ohio, with 79% of the community water systems, over 99% of the non-community water systems, and nearly 1 million rural homes utilizing ground water (OhioEPA, 2000). Arsenic concentrations in ground water above the MCL of 10 µg/L occur throughout Ohio, particularly in areas with sand and gravel aquifers (OhioEPA, 2000). In many instances treating As-containing ground water to meet regulatory needs and protect public health will require costly modifications to optimize existing treatment processes or the addition of point-of-use treatment techniques. The United States Environmental Protection Agency has issued guidance in selecting treatment methods for removing arsenic, and emerging technologies utilizing membranes (e.g., reverse osmosis), adsorptive processes (e.g., activated alumina), and precipitative processes (e.g., enhanced coagulation/filtration) show particular promise (Hering et al., 1997; Brandhuber and Amy, 2001). Common inorganic and organic ground water constituents reduce removal efficiency, and natural organic matter (NOM) decreases removal by 20 - 50 % (Hering et al., 1997; Brandhuber and Amy, 2001). Recent evidence suggests that NOM can complex arsenic to form stable solution complexes (Redman et al., 2002), and the increase in arsenic solubility resulting from the presence of such stable As-NOM complexes could be responsible for reduced removal efficiency. Details of these interactions are limited, however, and their importance is currently unknown. Knowledge of the fundamental processes that control As solubility, transport, and treatment, including interactions between arsenic and NOM, is crucial to maintaining the quality of ground water that approximately five million people in Ohio depend upon for their daily needs.

Nature and Scope of the Research

Arsenic (As) is a naturally occurring trace element in the earth's crust and is a common constituent in many igneous and sedimentary rocks. Arsenic is readily mobilized into solution through the combined effects of geochemical interactions and biological activity, and is normally present in surface and ground water at low concentrations (≤ 1 µg/L) (Welch et al., 2000; Smedley and Kinniburgh, 2002). Although high As concentrations are associated with

anthropogenic sources, the majority of environmental As problems are the consequence of natural processes (Welch et al., 2000; Smedley and Kinniburgh, 2002). Arsenic toxicity to humans is well documented (NRC, 1999), and its presence at elevated concentrations in the public water supply is of great contemporary concern (Nickson et al., 1998; NRC, 1999; Welch et al., 2000; Berg et al., 2001; Smedley and Kinniburgh, 2002).

In natural water systems, arsenic predominately exists in the inorganic form as oxyanions of trivalent arsenite, As(III), or pentavalent arsenate, As(V). Oxidizing conditions favor the formation of arsenate species (H_3AsO_4 , H_2AsO_4^- and HAsO_4^{2-}), whereas reducing conditions favor arsenite species (H_3AsO_3 and H_2AsO_3^-). The species H_2AsO_4^- , HAsO_4^{2-} and H_3AsO_3 prevail under environmental conditions, where the pH spans 4 to 9 (Baes and Mesmer, 1976). Although the redox state of a system is important, arsenic solubility and transport is dominated by adsorption reactions that occur at the surface of reactive iron and aluminum oxide minerals. Adsorption of arsenic oxyanions by mineral surfaces is favored at low pH, and adsorption decreases in magnitude with increasing pH in a manner consistent with other anions (Sigg and Stumm, 1981). In general, arsenate is adsorbed to a greater extent than arsenite, except at elevated pH (≥ 9) where the opposite occurs (Xu et al., 1988; Wilkie and Hering, 1996; Raven et al., 1998). Consequently, in most environmental systems arsenite is more mobile and bioavailable, hence more toxic than arsenate (NRC, 1999; Smedley and Kinniburgh, 2002).

Co-occurring anionic solutes alter the adsorption and thus the solubility of arsenic. Sulfate and phosphate directly compete with arsenic for surface sites on reactive metal oxides, particularly at low pH, and increase arsenic solubility (Xu et al., 1988; Manning and Goldberg, 1996; Wilkie and Hering, 1996); molybdate, however, has little net effect on As adsorption or mobility (Manning and Goldberg, 1996). Surface complexation models suggest that dissolved carbonate should interfere with arsenic adsorption on mineral surfaces at carbonate concentrations typically measured in ground and soil waters (Appelo et al., 2002). Experimental evidence in support of these calculations is still lacking because carbonate adsorption reactions are difficult to study (Wilkie and Hering, 1996).

The formation of solution complexes between arsenic oxyanions and other elements is limited (Cullen and Reimer, 1989), however, even such limited interactions still influence arsenic speciation (Lowenthal et al., 1977; Wilkie and Hering, 1996; Redman et al., 2002). For example, in artificial seawater arsenate forms ion pairs with magnesium and calcium (Lowenthal et al., 1977). These ion pairs result from charge screening that is induced by the high solution ionic strength and their presence increases the concentration of arsenic (Lowenthal et al., 1977). A similar process decreases arsenic solubility by enhancing As (V) adsorption at elevated pH (Wilkie and Hering, 1996) where the adsorption of calcium reduces unfavorable coulombic interactions that otherwise would limit the adsorption of arsenate oxyanions.

The adsorption of arsenate and arsenite to mineral surfaces is reduced in the presence of natural organic matter (NOM) (Xu et al., 1988; Xu et al., 1991; Howell, 1994; Grafe et al., 2001; Grafe et al., 2002; Redman et al., 2002). NOM is ubiquitous in aquatic systems and consists of a heterogeneous mixture of polyfunctional molecules of varying size and reactivity. The ability of NOM to bind contaminants and mineral surfaces can markedly alter contaminant mobility and has resulted in extensive research (e.g., Davis, 1984; Pignatello and Xing, 1996; McCarthy et al., 1998; Lenhart and Honeyman, 1999). The effects of NOM on As adsorption differ depending upon the NOM source, as well as the charging characteristics and surface area of the adsorbent mineral (Xu et al., 1988; Xu et al., 1991; Howell, 1994; Grafe et al., 2001; Grafe et al., 2002). Like sulfate and phosphate, the reduction in arsenic adsorption is presumed to result from

competition between As and NOM for surface sites (Xu et al., 1988; Xu et al., 1991; Bowell, 1994; Grafe et al., 2001; Grafe et al., 2002). Redman et al. (2002), however, present evidence that supports the formation of stable As-NOM solution complexes, which could be the reason for the reduced As adsorption. The complexation of As by NOM depended upon the NOM source and increased with NOM-bound cationic metals, particularly Fe (Redman et al., 2002).

A comprehensive framework for understanding the extent and importance of arsenic complexation by NOM in natural waters awaits development. Scant evidence, other than that presented by Redman et al. (2002), exists examining the formation of solution complexes between NOM and As (Tanizaki et al., 1985; Thanabalasingam and Pickering, 1986). Thanabalasingam and Pickering (1986) find that the association of As(V) and As(III) with two commercial humic acids followed a Langmuir relationship, and that NOM binds arsenate more strongly than arsenite. Tanizaki et al. (1985) sampled river water in Japan and report that approx. 60% of the As was associated with colloidal matter that consisted primarily of organic carbon. These results provide little additional insight into the complexation of As by NOM, and many questions remain, including the role of coexisting cationic solutes, the impact of solution pH, and the dependence of As complexation on the physicochemical properties of NOM.

Research Objective

The objective of this research is to investigate the association of inorganic arsenic with different sources of NOM in the presence of metal cations (e.g., Ca^{2+} , Mg^{2+} and Al^{3+}). Arsenic is highly toxic and readily mobilized in significant concentrations by natural processes that occur in ground water. The EPA considers arsenic to be a priority pollutant and recently lowered the MCL to 10 $\mu\text{g/L}$ from 50 $\mu\text{g/L}$. Preliminary results focused on examining interactions between As, metal cations, and NOM using capillary electrophoresis.

Materials and Methods

Stock solutions of arsenate (As(V)) and arsenite (As(III)) were prepared using sodium hydrogenarsenate heptahydrate, $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, and sodium metaarsenite, Na_3AsO_3 , respectively (both purchased from Aldrich). Water for all experiments was supplied from a Milli-Q water system ($>18 \text{ M}\Omega \times \text{cm}$ resistance, Millipore). Two samples of NOM were purchased from the International Humic Substances Society (Table 1); Suwannee River NOM (SRNOM) and Nordic Lake NOM (NLNOM). In this interim report we focus on results using SRNOM. The elemental composition of SRNOM (108 mg/L, pH 3.85) was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES; Varian) and graphite furnace atomic absorption spectrometry (GFAA; Varian) and confirmed the arsenic content in the sample was negligible (Table 2).

Table 1 - IHSS NOM Elemental Compositions and Stable Isotopic Ratios (%(w/w)).

Aquatic NOM	H ₂ O	Ash	C	H	O	N	S	P	¹³ C	¹⁵ N
Suwannee River	8.15	7.0	52.47	4.19	42.69	1.10	0.65	0.02	nd	Nd
Nordic Lake	nd	41.4	53.17	5.67	nd	1.10	Nd	nd	nd	Nd

Table 2 - Elemental Analysis of SRNOM (mg/g).

Al	As	Ba	Ca	Cu	Fe	K	Mg	Pb	S	Se	Si	Sr	Zn
0.85	nd*	<0.01	0.35	0.01	2.19	0.28	0.09	nd	2.90	nd	4.20	<0.01	1.44

* Limit of detection by GFAA for As is 0.9 µg/L

An HP^{3D} capillary electrophoresis (CE) system (Agilent Technologies, Inc.) with direct UV detection and normal electroosmotic flow (EOF) was used as the CE device to separate arsenate and arsenite. A fused-silica capillary of 50 µm i.d. × 48.5 cm was used in all experiments. The effective length of the capillary to the detector is 40 cm and the capillary temperature was maintained at 20°C. The separation voltage was set to +15 kV, although a range in values between +10 kV and +25 kV was investigated. Hydrodynamic injection at a pressure of 50 mbar was used for sample introduction and on-capillary UV diode-array was used for detection at a wavelength of 192 nm. (The minimum wavelength is 191 nm for the Agilent, diode-array with a deuterium lamp). The total injection time was 5 s or 10 s. To ensure uniform capillary surface conditions, the capillary was washed with a 0.1 M NaOH solution for 10 min at the beginning of each workday. Prior to each injection, the fused-silica capillary was flushed with 1 M NaOH for 1 min, Milli-Q water for 1 min and electrolyte buffer for 2 min.

Results

CE studies with Arsenite and Arsenate: The absorption of ultraviolet light by inorganic arsenic species increases as the wavelength is decreased below 250 nm and appears strongest near 190 nm. Sun et al. 2002 applied CE at a wavelength of 192 nm to measure arsenate and arsenite solutions down to approximately 1 to 6 mg/L. Under similar experimental conditions we measured arsenite at 5.2 min., but seemed unable to detect arsenate (Figure 1). Investigating further using a UV-VIS spectrophotometer (Shimadzu Co., Kyoto, Japan), we scanned arsenite and arsenate samples from a wavelength of 190 to 300 nm. For a 20 mg/L arsenite sample at pH 6.58 the maximum absorbance at a wavelength of 192.8 nm was 0.73; however, at the same wavelength the maximum absorbance of a 200 mg/L arsenate sample at a similar pH of 6.84 was only 0.12. Although this suggests that the low absorptivity of arsenate ($0.6 \text{ L cm}^{-1} \text{ g}^{-1}$) compared with arsenite ($36.5 \text{ L cm}^{-1} \text{ g}^{-1}$) might be responsible for our inability to detect arsenate additional work is necessary to confirm the actual cause. In the remainder of this report we focus on results obtained with arsenite.

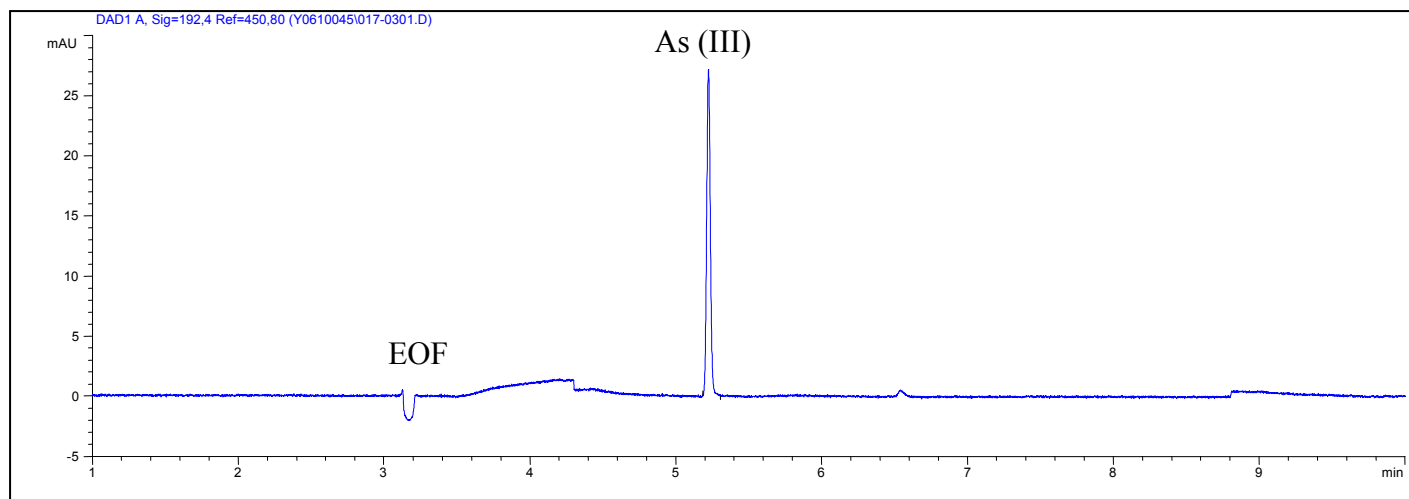


Figure 1. Electropherogram of arsenite (44.11 mg/L) in the borate buffer (20 mM, pH 10).

The ability of CE to separate analyte species is dependent upon a proper buffer selection. We tested four common buffer solutions; carbonate (20 mM, pH 10), borate (20 mM, pH 10), phosphate (20 mM, pH 5, 7, 9, 10, and 11), and acetate (20 mM, pH 7.3). Optimum separation of arsenite occurs at elevated pH where both borate and carbonate are the most effective buffers, but due to its lower UV background borate is a better choice than carbonate.

Studies examining the pH effect on arsenic and NOM complexation will be performed at different pH values and in preparation we investigated the influence of buffer pH on arsenite detection using phosphate buffers at pH 5, 7, 9, 10, and 11. At pH values of 5 and 7, the arsenite peak was very close to the EOF peak, indicating it will be difficult to accurately analyze the peak area. The pH of the electrolyte has a significant influence on the migration time of analytes and potentially the separation efficiency as well. Furthermore, it is possible that the electrophoretic mobility of arsenic is a weighed average of individual arsenic species. Careful attention to the ability of the buffer to impact migration times and separation efficiencies will be an important consideration for future experiments.

Evaluation of two-component interactions. Preliminary results examining interactions between arsenite and SRNOM were collected by mixing 5-mL aliquots of arsenite and SRNOM solutions in polyethylene tubes. The initial arsenite and SRNOM concentrations were 44 mg/L and 57.27 mg/L, respectively. The pH value was not recorded. Tubes were rotated in the dark for 24 hours at room temperature (25 °C). Blanks run in parallel ensured that adsorption of arsenite to the surface of the polyethylene tubes was negligible. After equilibration, the mixture of arsenite and SRNOM solution was analyzed using CE. The detection wavelength was fixed at 192 nm although the maximum absorbance of SRNOM was measured at 195.5 nm.

The peak in the electropherogram associated with As(III) exhibits a slight decrease (~ 3%) in the mixed arsenite-SRNOM sample (Figure 2a) compared with the peak in an NOM-free electropherogram at the same concentration (Figure 1). This we attribute to a decrease in the concentration of free arsenite anions due to the formation of a small amount of SRNOM-As(III) complexes. The arsenite peak in Figure 2a occurs simultaneously with an “NOM hump” in the arsenite-free SRNOM sample (Figure 3). Changes in the peaks associated with NOM also suggest the formation of As(III)-NOM complexes (Figure 2b). For example, the height of the NOM peak at 9 minutes, NOM C, decreases and splits in the presence of arsenite (Figure 2b)

which occurs, according to Nordén and Dabek-Zlotorzynska (1996), when complexes are formed with NOM. Note that the sharp peaks in the SRNOM electropherogram (NOM A, NOM B, and NOM C) and the broad NOM hump occur as a result of the heterogeneity and polydispersity of NOM. NOM macromolecules span a range in size and functional group content, and thus exhibit nonuniform charge-to-mass ratios and electrophoretic mobilities. In general, during normal EOF molecules having more negative charge-to-mass ratios also have greater electrophoretic mobilities and longer migration times.

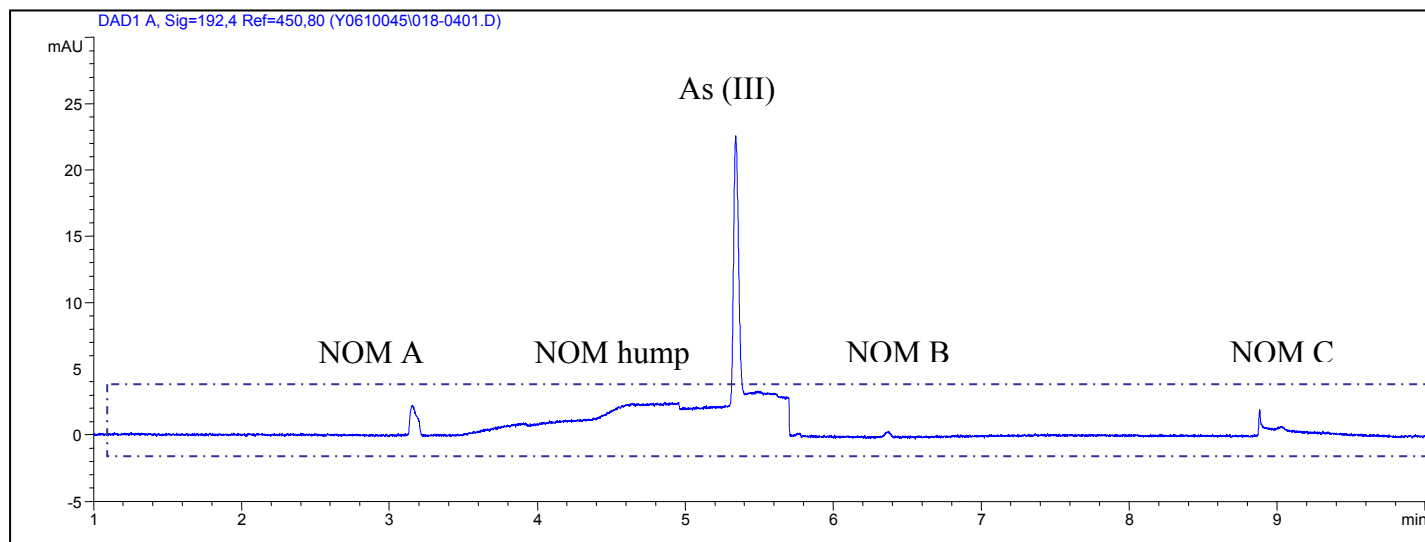


Figure 2a. Electropherogram of arsenite and SRNOM (20 mM borate, pH 10).

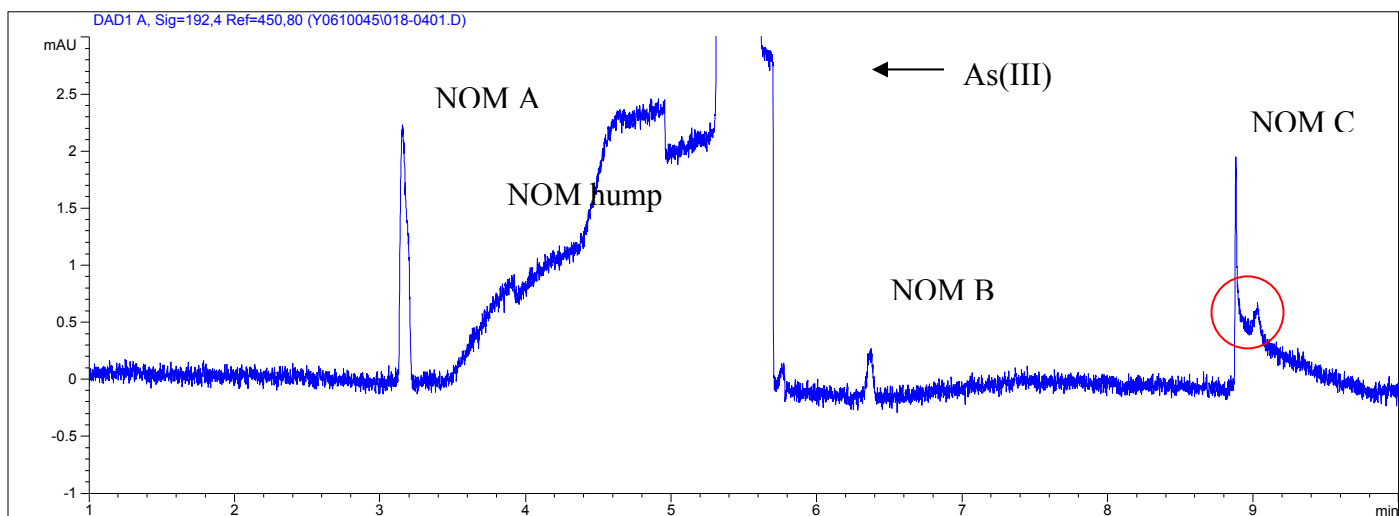


Figure 2b. Exaggeration of lower absorbance region in the electropherogram of arsenite and SR-NOM mixture in the borate buffer (Figure 2a).

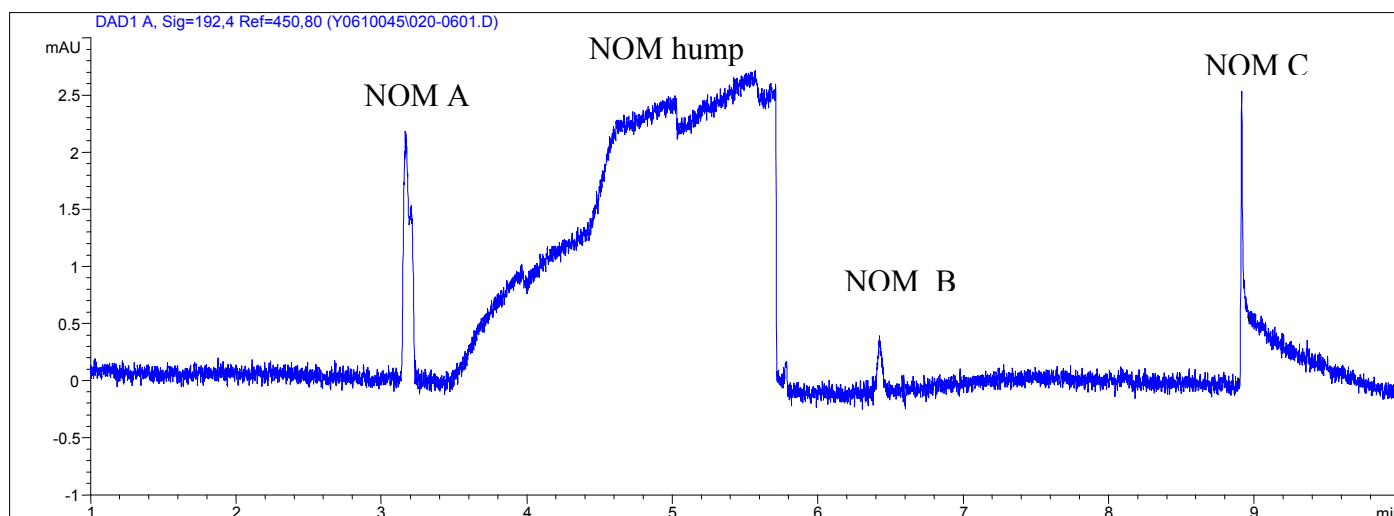


Figure 3. Electropherogram of SR-NOM (57.27 mg/L) in the borate buffer (20 mM, pH 10).

Future Research

Work continues with SRNOM, varying pH, and constituent ratios. The cationic impurities in SRNOM (see Table 2) will be removed for future measurements. Similar experiments are planned for NLNOM, which must also be cleansed of the large ash content (Table 1). Experiments to examine the acid-base characteristics and pH-dependence of As-NOM interactions will also be conducted.

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